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MECHANOCHEMICAL SYNTHESIS OF MULLITE

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The specifics of mechanical activation processes in modifying synthetic corundum powder and gels by silicon alkoxide are considered. As Al_2O_3 is milled with a silicon alkoxide additive, Al_2O_3 and SiO_2 reactants are activated with the formation of an intermediate self-organized complex, in which the mechanochemical interaction proceeds accompanied by the formation of mullite.

The mechanicochemical method for activation of solid-phase reactions is becoming more common [1]. The practical use of mechanical activation is ahead of the theoretical studies of mechanicochemical processes, including the synthesis of new formations in such systems. The mechanisms of these processes have not yet been reliably identified, and an empirical approach prevails in the choice of modifying additives and the optimum conditions for their application. This approach is based on experimental data resulting from the study of the process of pulverizing different powders with additives of surfactants, organoelemental, and other compounds and investigation of the variations in the phase composition of the modified powders.

Tribochemical (mechanochemical) reactions, despite the fact that they do not quite agree with the classical thermodynamics, really exist, which was substantiated by our research [2 – 4] as well. It was found that amorphous SiO_2 in a modifying additive takes part in mechanicochemical and high-temperature reactions (their intensity is not unambiguous), resulting in the emergence of seeds of various new formations [5]. The local area of contact of the milling bodies [6, 7] exhibits not only the highest compressive stresses but also a substantial increase in temperature compared to the temperature inside the milling chamber. As a consequence of the effect of mechanical stresses and the high local temperatures, crystal lattices of modified powders are disturbed, and organic substance gets transformed, including pyrolysis, hydrolysis, and mechanical and thermal destruction of organoelemental matter, which results in the formation of highly active amorphous silica and carbon [8].

The purpose of the present work is to study the process of mechanical synthesis of mullite in the course of modification of synthetic corundum by silicon alkoxide.

Gels of silicon alkoxide hydrolyzed by a stoichiometric quantity of water are amorphous varieties of silica [3 – 5]. Gels are attributed to the series of intermediate supermolecular isomers of the β-cristobalite type [9]. Amorphous silica is metastable. Metastable varieties of SiO_2 also include coesite and stishovite; the rest of the silicon modifications are thermodynamically stable at normal temperatures. Polymorphic modifications of SiO_2 have different and energetically nonequivalent structures. This determines their chemical activity.

The use of amorphous silica is the most effective in the intensification of sintering processes and phase formation; therefore, it is expedient to preserve the amorphous state of silica when using gel in ceramic technologies. It is established that SiO_2 in gels under different conditions undergoes different transformations. As gel is milled with modifying additives in mixture preparation, i.e., already in the course of modification, silica is partly crystallized, and after 6 h of milling a peak of α-quartz [4], i.e., one of the high-temperature modifications of SiO_2, is registered.

With the increasing duration of gel milling together with the silicon alkoxide additive, the intensity of α-quartz reflection increases and the peak width decreases, i.e., the crystallization process continues. This is confirmed by the fact that gel in the course of pulverization receives energy, which facilitates the near-order rearrangement of the supermolecular structure and promotes transformations resulting in the formation of α-quartz crystals out of amorphous silicon gel, i.e., a mechanochemical transformation of SiO_2 takes place.

This process differs from the processes in heat treatment of gel [8] and gel milling without additives (Fig. 1*a*, *b*). In both cases, silica preserves its amorphous state up to higher temperatures, and under high rates of temperature rise and heat treatment it starts transforming into β-cristobalite only at 1713 K (Fig. 1*c*). When silicon alkoxide is used as a mod-

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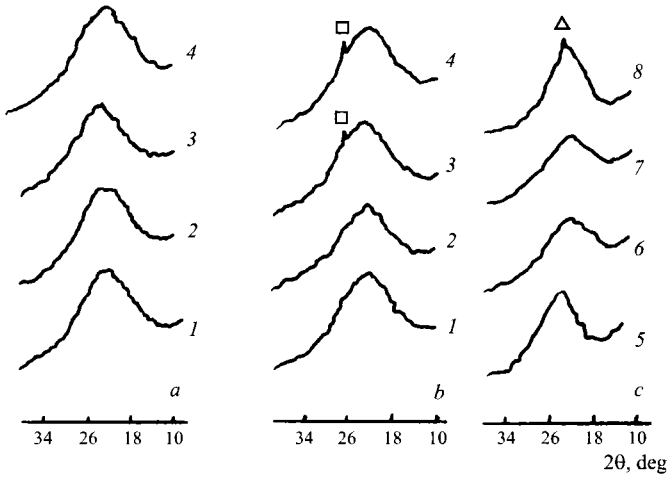

Fig. 1. Diffraction patterns of pulverized gel without additives (*a*) and modified with silicon alkoxide additives (*b*) for 1 h (*1*), 6 h (*2*), 12 h (*3*) and 24 h (*4*), as well as gel heat-treated at temperatures of 293 K (*5*), 1173 (*6*), 1173 (*7*), and 1713 K (*8*). △) β-cristobalite; □) α-quartz.

ifying additive in gel pulverizing, there is no substantial increase in the amorphism of silicon powder, since the halo areas in the diffraction patterns (Fig. 1*a*, *b*) are virtually equal.

In heat treatment of non-pulverized gel, the degree of amorphism of ultradisperse SiO_2 is slightly decreased (Fig. 1*b*). The structure of ultradisperse silica in all cases is sufficiently amorphous, and the synthesized crystal phases (α-quartz, β-cristobalite) are present in insignificant quantities.

The phase emerging from silica in mechanical activation of gel is α-quartz, and heat treatment of the initial gel produces β-cristobalite. Based on the emerging crystalline phases of SiO_2 in modification of α-Al_2O_3, one can identify the prevailing process or the presence of these two processes of SiO_2 transformation from silicon alkoxide during the modification of high-melting powders.

Modification of synthetic corundum by silicon alkoxide was carried out in the course of its pulverizing in a ball mill of 5-liter capacity with a rotational speed of 79 min^{-1} and a powder : balls ratio equal to 1 : 3. The milling duration ranged from 1 to 60 h. Sampling of powder was performed at prescribed time intervals. The size of synthetic corundum grains was studied with a Sedigraph instrument and an MIN-8 microscope. Samples of modified synthetic corundum were subjected to DTA, x-ray phase analysis, and Raman spectroscopy (RS).

For the purpose of determining the degree of amorphization of electrocorundum surface after its modification with silicon alkoxide, synthetic corundum samples subjected to mechanical activation and subjected to milling without additives were treated with a mixture of 0.1 N HCl and HNO_2 acid for 24 h at a temperature of 293 K, with constant stirring for the first three hours of dissolution. The precision of determining the amount of the dissolved part of the sample was 0.01%.

The x-ray phase analysis of the samples was carried out on a DRON-3 unit with CuK_α radiation. Mullite was synthesized from gel based on silicon alkoxide and aluminum oxychloride with a preset ratio of Al_2O_3 : SiO_2 equal to 3 : 2 [10]. Spectroscopic studies were carried out on a MOLE instrument (France). The RS spectra of the mullite synthesized by the sol-gel method were used to identify the mullite produced by the mechanochemical method.

The solid-phase reaction of mullite synthesis implies the formation of a catalytically active intermediate complex, including both reactants with the required ratio of cybotaxic groups. The increase in the activity of the reactants is due to mechanochemical processes. A special role in these processes is played by the transformations of silicon alkoxide and gel, as well as the corundum grain surface and the defectiveness of the crystalline structure of α-quartz. We should also note the significant role of the steric factor and absorption interaction between the modifying additives and the surface of the milled powder.

The study revealed that the process of modification of high-melting powders, including synthetic corundum, using silicon alkoxide additive is accompanied by the process of transformation of the high-melting powder and the organoelemental compound [11]: pyrolysis of silicon alkoxide and its hydrolysis and mechanical destruction of the products of silicon alkoxide hydrolysis (similar to the thermal destruction of gel with the formation of carbon clathrates in SiO_2), as well as variations in the dispersion and morphology of α-Al_2O_3 particles (accompanied by increased defectiveness of the structure of α-Al_2O_3 polycrystals, amorphization of the grain surface, and more active interaction with the amorphous silica based on silicon alkoxide).

The nanometric amorphous silica formed as a result of silicon alkoxide pyrolysis is distributed in an extremely thin layer over the surface of synthetic corundum rendered amorphous.

In the first hours of modification of powders using silicon alkoxide, one can observe an increase in the level of defects of the structure of α-Al_2O_3 polycrystals. The structural modifications are identical [2, 12] when using various quantities of modifying additives (1 – 3%), and the dispersion of powder is slightly decreased, which is related to the agglomeration of particles as a result of sol formation under the hydrolysis of silicon alkoxide with the water released in its partial pyrolysis.

Particle agglomerates in time attain a size from 10 to 150 μm, and their quantity does not exceed 25% after 6 and 60 h of milling, whereas the agglomerates contain over 95% single particles 1 ± 0.5 μm in size. The quantity of aggregates more than 30 μm in size attains 35 – 40% (Fig. 2). Agglomeration of finely dispersed powder accelerates the involvement of the products of mechanical and thermal destruction of silicon alkoxide, which is evidenced by the decreased weight losses

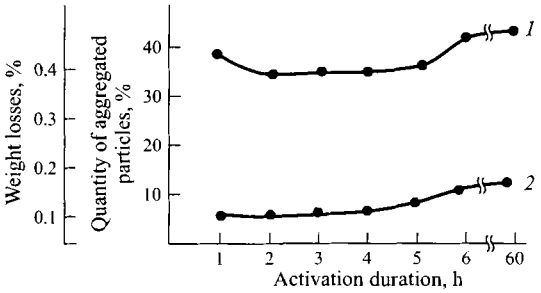

Fig. 2. Dependence of the quantity of aggregated particles over 30 μm in size (*1*) and weight losses (*2*) of modified synthetic corundum on the duration of mechanical activation.

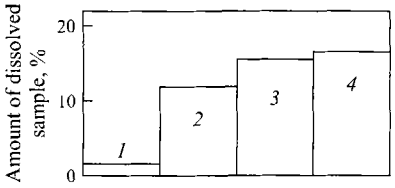

Fig. 3. Amount of dissolved part of the powder versus the quantity of the modifying agent after mechanical activation for 60 h.

and increased temperature of gel decomposition from 433 to 503 K.

As synthetic corundum is modified, its grain surface is activated, with formation of β-Al_2O_3 on the surface of α-Al_2O_3 grains. The amorphous layer on the grain surface is more easily dissolved in acid solution than α-Al_2O_3. As the amount of modifying additive increases, the amount of the dissolved part of the synthetic corundum samples becomes greater, which is due to the increase in the amorphous part of the surface (Fig. 3). The x-ray phase analysis of the modified powders established that while synthetic corundum is milled with modifying additives, apart from the α-Al_2O_3 peaks in the diffraction patterns, first β-Al_2O_3 arises, and after 2 h of milling, SiO_2 in silicon alkoxide becomes partly crystallized. At the same time, the x-ray-amorphous halo is kept at the same level for modified powders for 1 – 6 h (Fig. 4). It is likely that the temperature in the contact zone of the milling bodies inside the ball mill attains high values. Similar to the vibration mill, it can attain 2071 K [6].

The high temperatures result in the mechanical destruction of silicon alkoxide, thermal transformation of gel based on silicon alkoxide, and solid-phase reactions producing compounds which are usually formed under high firing temperatures. The presence of the α-quartz and β-cristobalite peaks in the diffraction patterns of modified powders, along with the amorphous silica phase in the first 6 h of milling, is evidence of the presence of the transformation products of mechanical activation (α-quartz) and thermal destruction (β-cristobalite) of silicon alkoxide and gel under the effect of mechanical stresses and pressure, which together with amor-

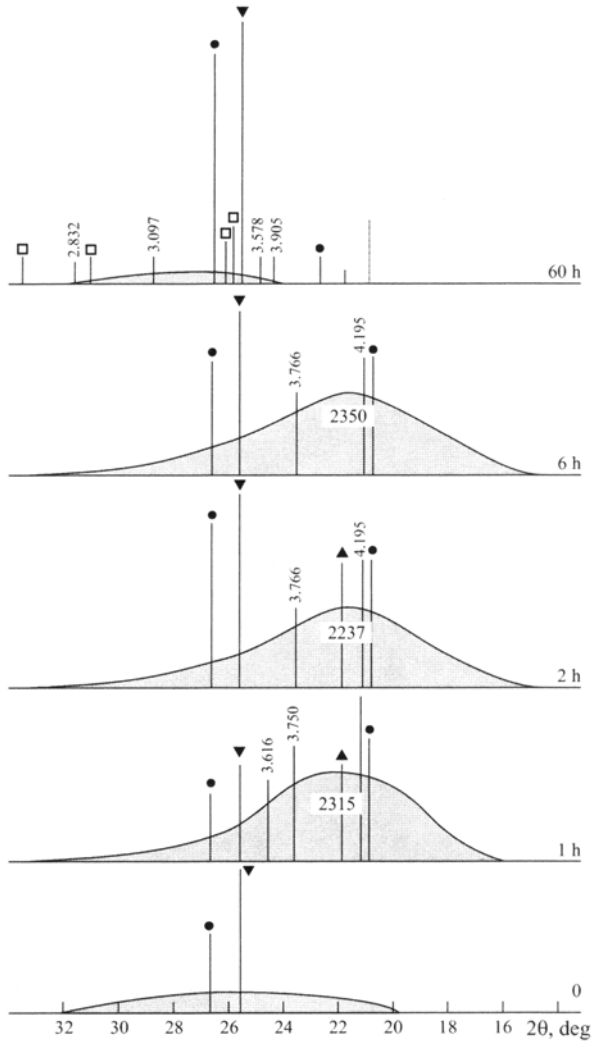

Fig. 4. Variation in the phase peak intensity on diffraction patterns of synthetic corundum modified with silicon alkoxide (1%) in mechanical activation. ▼) Al_2O_3; ●) quartz; □) mullite; ▲) β-cristobalite.

phous SiO_2 are involved in the mechanochemical synthesis of several new compounds.

Seeds of mullite or mullite-like phase are formed in the course of modification of α-Al_2O_3 powder. It is likely that an the moment of a concentrated impact, near-order self-organization takes place at the sites of α-Al_2O_3 disordered structure and the surface of its grains together with amorphous SiO_2 arranged in a near contact with them, which self-organization is directed toward the formation of AlO_4, AlO_6, and SiO_4 groups in a proportion needed for mullite synthesis. All this ensures the synthesis of the mullite phase $3Al_2O_3 \cdot 2SiO_2$, stable at normal temperatures and structurally perfect, in an amount sufficient for its identification by x-ray phase analysis. This mechanochemical effect, in our opinion, is a consequence of the high local pressures and temperatures at the point of co-impact of the milling bodies, between which the

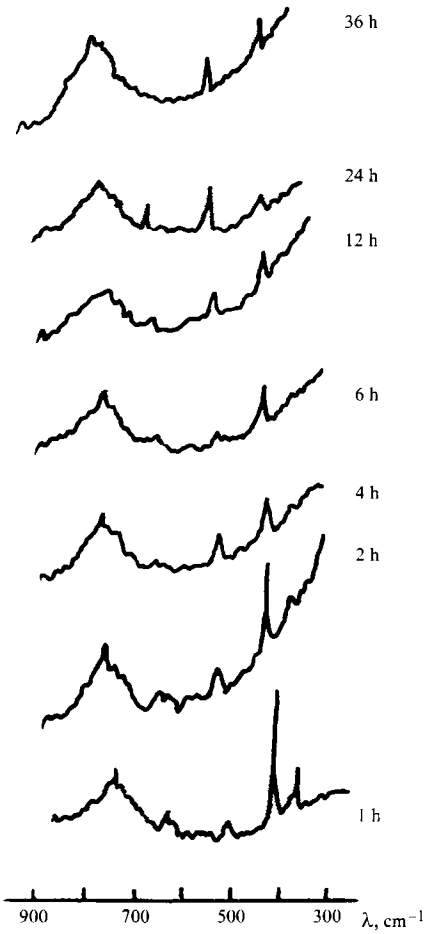

Fig. 5. Raman spectra of modified synthetic corundum.

highly defective and amorphous corundum coated with disperse SiO_2 is situated.

An evidence of mullite formation as a consequence of mechanochemical reactions during the modification of synthetic corundum by silicon alkoxide are the RS data for the obtained powder (Fig. 5). The absorption band typical of α-Al_2O_3 on the RS spectrum (in the region of 400 cm^{-1}) decreases in the course of mullite sintering. The absorption band of mullite vibrations (in the region of 750 cm^{-1}), which emerges in the first hour of mechanical activation and is preserved during the entire modification period, corresponds to such a band in the RS spectrum of mullite synthesized by the sol-gel method. Synthetic corundum powder after modification consists of α-Al_2O_3 and mechanically synthesized phases (mullite and others).

The formation of mullite is confirmed by various methods. Since the new phase arises in mechanochemical synthesis in the temperature range $(0.2 - 0.3)T_m$ subject to the obligatory condition of component interaction at the molecular or atomic level, the presence of mullite peaks on the diffraction patterns of modified α-Al_2O_3 powders points to such deep processes of distribution of highly active components Al_2O_3 and SiO_2 and their interactions which are required for the synthesis of mullite, i.e., which satisfy the above condition.

Thus, the high defectiveness of the structure of milled corundum powder, the amorphous state of the grain surface, and the amorphism of ultradisperse silica which emerges as a result of mechanical activation in modifying synthetic corundum powders with silicon alkoxide lead to the mechanochemical synthesis of a metastable mullite phase.

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